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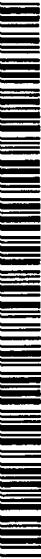
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(71) Applicant and
(72) Inventor: COLLINS, Hugh, Frederick [GB/GB]; 4 Myrtle Grove, Waterloo, Liverpool L22 2AG (GB).

(74) Agent: W.P. THOMPSON & CO.; Coopers Building, Church Street, Liverpool L1 3AB (GB).

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(54) Title: REJUVENATION AND/OR CLEANING OF CATALYSTS

WO 01/94013 A1

(57) **Abstract:** One aspect of the invention provides a rejuvenating and/or cleaning composition for a catalyst of a vehicle catalytic converter, comprising at least one hydrocarbon source and at least one oxygen donor. The inventive composition can also comprise a hydrocarbon source and an oxygen donor wherein said composition generates an organic acid vapour on combustion. Preferably, the inventive compositions comprise one or more organic solvents selected from isopropyl alcohol, acetone, xylene and paraffin (kerosene). The invention also provides a method of rejuvenating and/or cleaning a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle, said method comprising: (i) bringing the catalytic converter up to working temperature; and then (ii) passing the aforementioned compositions into an engine of the vehicle whilst running the engine at idle. A similar method comprises: (i) bringing the vehicle engine to working temperature; (ii) disconnecting the vehicle's fuel line from the engine; (iii) connecting the engine to a means for feeding any rejuvenating and/or cleaning composition thereto; and (iv) feeding the cleaning composition into the engine whilst the engine is running at a temperature high enough to effect cleaning of the catalyst. The atmosphere. Another aspect of the invention provides a method of rejuvenating and/or cleaning a catalyst of a vehicle catalytic converter without removal of the catalyst from the vehicle, the vehicle having an engine and a fuel tank, said method comprising the steps of: (i) introducing the cleaning composition into the fuel tank, said tank already containing a quantity of fuel; and then (ii) running the engine of the vehicle to effect cleaning of the catalyst.

REJUVENATION AND/OR CLEANING OF CATALYSTS**BACKGROUND OF THE INVENTION**

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1. Field of the Invention

The present invention relates to a rejuvenating and/or cleaning agent, particularly to a rejuvenating and/or cleaning agent for a catalyst of the type used in a vehicle catalytic converter, and to a method of rejuvenating and/or cleaning the catalyst of a catalytic converter.

2. Brief Description of the Prior Art

Catalytic converters are now fitted to most internal combustion engine vehicles, in order to reduce the levels of undesirable components in exhaust emissions. In particular, exhaust emissions of carbon monoxide (CO), unburnt fuel hydrocarbon (HC) and nitrogen oxides (NO_x) are regulated by law.

A catalytic converter usually comprises a noble metal catalyst, for example of platinum, palladium and/or rhodium, which converts undesirable unburnt hydrocarbons (HC) and carbon monoxide (CO) to carbon dioxide and water, and nitrogen oxides (NO_x) to nitrogen and water.

Typically, a catalytic converter consists of a cordierite ceramic monolith extruded to form a honeycomb-like structure of cells having a large surface area. The cell walls are coated with the metal catalyst, such that the engine exhaust gases contact the catalyst surface prior to their emission into the atmosphere. Alternatively, the noble metal catalyst may be dispersed on a high surface area carrier in the form of alumina pellets.

A major problem with catalytic converters is that the

catalyst is easily poisoned and/or rendered less effective, for example by a build up of carbonaceous deposits, or by the accumulation of certain elements such as lead or phosphorus on the surface of the catalyst..

5 A number of processes have been employed for restoring the activity of the catalyst. Most, however, require the catalyst to be removed from the vehicle. One such method is described in European Patent Application EP 0178792 A, which discloses a method of regenerating a
10 phosphorus-poisoned exhaust catalyst by washing or soaking the catalyst in an acid solution and then heating the wetted catalyst in air.

There have also been attempts to overcome the problem of catalyst poisoning without removing the catalyst from
15 the vehicle. For example, European Patent Application EP 0070619 A describes a method of regenerating a catalyzed particulate filter by occasionally supplying an amount of unburnt fuel to the filter in order to ignite particulates deposited in the filter. PCT Application WO 97/41336 and
20 British Application GB 2328626 describe an apparatus and a method for regenerating a diesel engine NO_x catalyst which has been contaminated with SO_x, by adding a predetermined quantity of a reductant diesel fuel to the exhaust pipe via a special nozzle.

25 US Patent 5,316,558 to Gonzalez discloses a petroleum-derived fuel composition of improved efficiency which reduces the tendency of the fuel to create deposits, thus reducing exhaust emissions. There is no suggestion, however, that the disclosed compositions might serve to
30 regenerate a catalyst which has already been poisoned or affected by contaminants.

SUMMARY OF THE INVENTION

effective in the rejuvenation and/or cleaning of catalysts in catalytic converters of both gasoline and diesel-burning vehicles. Further experiments were carried out in which the composition of the agent was varied, and, for 5 the "in-tank" method of Examples 6 and 7, in which the ratio of composition added to the amount of fuel in the tank was varied. These compositions and methods gave similar results to those of the above Examples, though in most cases either a longer treatment time was required, or 10 a less pronounced reduction in emissions resulted.

Possible substitutes for the constituents are as follows:

	<u>Original component</u>	<u>Substitute</u>
	xylene	toluene, benzene
15	acetone	Methyl ethyl ketone, cyclohexane, acetone, alcohol
	isopropyl alcohol	ethanol
	kerosene	distillate white spirit

20 The above Examples are merely illustrative and non-limiting in scope, serving to indicate preferred embodiments of the invention only. It should be understood that variants of the invention are envisaged 25 without departing from the scope of the claimed invention.

References

1. Protection of Environment. Code of Federal Regulations, Parts 81-99 revised as of July 1, 1986. Fed Regist. 1986.
- 30 2. Statens naturvårdsverks författningsamling. SNFS 1992:4 MS:45. Kungörelse med föreskrifter om avgasrenig för lätta bilar. A14-Regulation.

I claim:

1. A rejuvenating and/or cleaning composition for a catalyst of a vehicle catalytic converter, comprising at least one hydrocarbon source and at least one oxygen donor.
2. A rejuvenating and/or cleaning composition as claimed in claim 1 wherein said composition generates an organic acid vapour on combustion.
3. A rejuvenating and/or cleaning composition as claimed in claim 2, wherein the organic acid vapour includes a carboxylic acid vapour.

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4. A rejuvenating and/or cleaning composition as claimed in claim 1, wherein the oxygen donor or one of the oxygen donors and the hydrocarbon source or one of the hydrocarbon sources are one and the same compound.

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5. A rejuvenating and/or cleaning composition as claimed in claim 1, including one or more organic solvents as hydrocarbon source and/or oxygen donor.

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6. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents include aliphatic alcohols, ketones, aromatic hydrocarbons and/or aliphatic hydrocarbons.

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7. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents include isopropyl alcohol.

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8. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents

include acetone.

9. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents 5 include xylene.

10. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents include isopropyl alcohol, acetone and xylene.

10 11. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents include alkanes, paraffin (kerosene) and/or lamp oil.

15 12. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents are selected from isopropyl alcohol, acetone, xylene and paraffin.

20 13. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims comprising isopropyl alcohol, acetone, xylene and paraffin.

25 14. A rejuvenating and/or cleaning composition as claimed in claim 13, comprising 10-40 wt% isopropyl alcohol, 10-40 wt% acetone, 35-65 wt% xylene and 5-15 wt% paraffin.

15. A rejuvenating and/or cleaning composition as claimed in claim 13, comprising 15-25 wt% isopropyl alcohol, 15-25 30 wt% acetone, 45-55 wt% xylene and 7-12 wt% paraffin.

16. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims, comprising one or more trace elements selected from Sr, Bi, Cd, Ba, Ni, Mn, Fe, 35 Na, Zn, Al, Ca, Cu, Pb, Co, K, Cr, Mg, As, Sn, Sb, V, Ti,

Be, Si, P, W, and Mo.

17. A rejuvenating and/or cleaning composition as claimed in claim 16, wherein those trace elements which are present are each present in an amount of \pm 30% of the figures shown for the respective element: Sr (0.01ppm), Bi (0.05ppm), Cd (0.01ppm), Ba (0.01ppm), Ni (0.07ppm), Mn (0.05ppm), Fe (0.16ppm), Na (4.03ppm), Zn (0.05ppm), Al (0.19ppm), Ca (0.14ppm), Cu (0.02ppm), Pb (0.06ppm), Co (0.01ppm), K (15.59ppm) Cr (0.01ppm), Mg (0.05ppm), As (0.05ppm), Sn (0.34ppm), Sb (0.10ppm), V (0.07ppm), Ti (0.01ppm), Be (0.01ppm), Si (0.39ppm), P (0.17ppm), W (0.14ppm), and Mo (0.01ppm).

15 18. The use of a rejuvenating and/or cleaning composition as defined in claim 1 to rejuvenate and/or clean a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle.

20 19. A method of rejuvenating and/or cleaning a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle, said method comprising:

25 (i) bringing the catalytic converter up to working temperature; and then
(ii) passing a rejuvenating and/or cleaning composition as defined in claim 1 into an engine of the vehicle whilst running the engine at idle.

30 20. A method as claimed in claim 19, wherein the rejuvenating and/or cleaning composition is passed into the vehicle engine under pressure.

35 21. A method as claimed in claim 19, the method further

comprising:

(i) bringing an engine of the vehicle to working temperature;

5 (ii) disconnecting the vehicle's fuel line from the engine;

(iii) connecting the engine to a means for feeding a rejuvenating and/or cleaning composition thereto; and

10 (iv) feeding the cleaning composition into the engine whilst the engine is running at a temperature high enough to effect cleaning of the catalyst.

22. A method of rejuvenating and/or cleaning a catalyst of a vehicle catalytic converter without removal of the catalyst from the vehicle, the vehicle having an engine and a fuel tank, said method comprising the steps of:

(i) introducing an amount of rejuvenating and/or cleaning composition into the fuel tank, said tank already containing a quantity of fuel; and then

20 (ii) running the engine of the vehicle to effect cleaning of the catalyst.

23. A method as claimed in claim 21, wherein the amount of composition added is predetermined by the quantity of fuel contained in the tank, and wherein the amount of composition added is in the range of 0.5 to 0.75 litres per 30 litres of fuel.

24. A method as claimed in claim 21, wherein the vehicle is run at a temperature of between 60 and 90°C.

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25. A method as claimed in claim 21, wherein the rejuvenating and/or cleaning composition is as defined in claim 1.

35 26. A method as claimed in claim 25, wherein the

rejuvenating and/or cleaning composition is combustible.

27. A method as claimed in claim 25, wherein the rejuvenating and/or cleaning composition is as defined in
5 claims 1.

28. A method as claimed in claim 25, wherein the vehicle is run at a temperature of between 60 and 90°C.

10 29. A method as claimed in claim 25, wherein the rejuvenating and/or cleaning composition is fed into the injection system, through the engine, through the catalytic converter and out through the exhaust system into the atmosphere.

INTERNATIONAL SEARCH REPORT

In national Application No
PCT/GB 00/04187A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J38/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 419 121 A (SUNG SHIANG ET AL) 30 May 1995 (1995-05-30) claims 1,12,13 ---	1-6,11, 12,19-29
X	EP 0 405 310 A (DEGUSSA) 2 January 1991 (1991-01-02) claims 1,7 ---	1-6,11, 12,18-29
X	US 5 316 558 A (GONZALEZ FRANK) 31 May 1994 (1994-05-31) claim 1 ---	1-6, 19-29
X	US 5 266 082 A (SANDERS JAMES K) 30 November 1993 (1993-11-30) claims 1,4 ---	1-8 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

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"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schwaller, J-M

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/GB 00/04187

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 748 289 A (DOUGLAS ALLAN S) 31 May 1988 (1988-05-31) examples 9,11 -----	1-8
X	US 5 314 851 A (HUBA FRANCIS) 24 May 1994 (1994-05-24) column 5, line 34 -column 5, line 35; claim 1 -----	1-7, 18-29
X	US 5 141 524 A (GONZALEZ FRANK) 25 August 1992 (1992-08-25) claim 1 -----	1-7,11, 12,19,22
X	US 5 688 295 A (YANG CHUNG-HSIEN) 18 November 1997 (1997-11-18) claim 1 -----	1-6,19, 22
X	US 4 405 336 A (BADGER STEPHEN L) 20 September 1983 (1983-09-20) claim 1 -----	1-12
X	FR 2 493 863 A (INST FRANCAIS DU PETROL) 14 May 1982 (1982-05-14) claims 1-4 -----	1-12

INTERNATIONAL SEARCH REPORT
Information on patent family members

In
tional Application No
PCT/GB 00/04187

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5419121 A	30-05-1995	AT	166699 T	15-06-1998
		AU	6405694 A	08-11-1994
		DE	69410608 D	02-07-1998
		DE	69410608 T	03-12-1998
		EP	0696337 A	14-02-1996
		JP	8509044 T	24-09-1996
		WO	9424424 A	27-10-1994
EP 0405310 A	02-01-1991	CN	1048581 A	16-01-1991
		JP	3096611 A	22-04-1991
		ZA	9004363 A	27-03-1991
US 5316558 A	31-05-1994	US	5141524 A	25-08-1992
		US	5433756 A	18-07-1995
US 5266082 A	30-11-1993	AU	4281893 A	18-11-1993
		MX	9302201 A	31-03-1994
		WO	9321286 A	28-10-1993
US 4748289 A	31-05-1988	NONE		
US 5314851 A	24-05-1994	CA	2113672 A,C	22-12-1994
US 5141524 A	25-08-1992	US	5433756 A	18-07-1995
		US	5316558 A	31-05-1994
US 5688295 A	18-11-1997	US	5931977 A	03-08-1999
US 4405336 A	20-09-1983	US	RE33562 E	02-04-1991
FR 2493863 A	14-05-1982	DE	3143654 A	08-07-1982
		SE	8106563 A	08-05-1982

REJUVENATION AND/OR CLEANING OF CATALYSTS

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Inventor(s): COLLINS HUGH FREDERICK (GB)

Applicant(s): COLLINS HUGH FREDERICK (GB)

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Equivalents: AU1155601, EP1289656

Cited Documents: US5419121; EP0405310; US5316558; US5266082; US4748289; US5314851; US5141524; US5688295; US4405336; FR2493863

Abstract

One aspect of the invention provides a rejuvenating and/or cleaning composition for a catalyst of a vehicle catalytic converter, comprising at least one hydrocarbon source and at least one oxygen donor. The inventive composition can also comprise a hydrocarbon source and an oxygen donor wherein said composition generates an organic acid vapour on combustion. Preferably, the inventive compositions comprise one or more organic solvents selected from isopropyl alcohol, acetone, xylene and paraffin (kerosene). The invention also provides a method of rejuvenating and/or cleaning a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle, said method comprising: (i) bringing the catalytic converter up to working temperature; and then (ii) passing the aforementioned compositions into an engine of the vehicle whilst running the engine at idle. A similar method comprises: (i) bringing the vehicle engine to working temperature; (ii) disconnecting the vehicle's fuel line from the engine; (iii) connecting the engine to a means for feeding any rejuvenating and/or cleaning composition thereto; and (iv) feeding the cleaning composition into the engine whilst the engine is running at a temperature high enough to effect cleaning of the catalyst. The atmosphere. Another aspect of the invention provides a method of rejuvenating and/or cleaning a catalyst of a vehicle catalytic converter without removal of the catalyst from the vehicle, the vehicle having an engine and a fuel tank, said method comprising the steps of: (i) introducing the cleaning composition into the fuel tank, said tank already containing a quantity of fuel; and then (ii) running the engine of the vehicle to effect cleaning of the catalyst.

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UK Patent Application GB 2 333 048 A

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(71) Applicant(s) Hugh F Collins 26 Oak Street, Upper Weedon, Northampton, NN7 HRQ, United Kingdom	(52) UK CL (Edition Q) B1E EG E1111 E1180 C5G GAC G101 G102 G132 G137 G175
(72) Inventor(s) Hugh F Collins	(56) Documents Cited EP 0178732 A2 EP 0166006 A1 EP 0070619 A2 WO 97/41336 A1 US 5316558 A US 4265638 A US 4147136 A
(74) Agent and/or Address for Service W P Thompson & Co Coopers Building, Church Street, LIVERPOOL, L1 3AB, United Kingdom	(58) Field of Search UK CL (Edition Q) B1E EG , C5G GAC INT CL ⁶ B01D 53/96 , B01J 38/00 , C10L 1/02 , F01N 3/20 Online databases: EPODOC, JAPIO and WPI

(54) Abstract Title
A composition for regenerating a catalytic converter

(57) A composition, which may be used in situ while the engine is running, comprises an oxygen donor and a source of hydrocarbon. The preferred composition contains xylene, isopropanol and acetone, together with one or more metallic trace elements.

The composition may be fed to the running engine, interrupting the normal fuel supply.

GB 2 333 048 A

DESCRIPTION

A REJUVENATING AND/OR CLEANING AGENT

The present invention relates to a rejuvenating and/or cleaning agent, and more particularly to a rejuvenating and/or cleaning agent for a catalyst of the type used in a vehicle catalytic converter, and to a method of rejuvenating and/or cleaning the catalyst of a vehicle's catalytic converter.

Catalytic converters are now fitted to most internal combustion engines, (e.g. petrol engine) vehicles. The catalytic converters usually comprise a precious metal catalyst, for example, the noble metals such as platinum and/or rhodium, which catalyst initiates conversion of harmful exhaust emissions such as, for example, nitrogen oxides, carbon monoxide and hydrocarbons into less harmful products such as, for example, carbon dioxide, nitrogen and water.

However, these catalysts are easily poisoned and/or are rendered less effective by, for example, a build up of carbonaceous deposits on the catalysts surface.

A number of processes for rejuvenating and/or cleaning catalysts are known. Most, however, require the catalyst to be removed from the vehicle.

It is an aim of the present invention to develop a composition and method for cleaning or

rejuvenating a catalyst of the type found in a catalytic converter of a vehicle without having to remove it from the vehicle.

The applicants have determined that a catalyst in a vehicle catalytic converter can be rejuvenated and/or cleaned in situ by passing a cleaning composition, preferably under pressure, into the vehicle engine whilst running the engine at idle, the catalytic converter having first been brought up to working temperature.

According to a first aspect of the present invention there is provided a method of rejuvenating and/or cleaning a catalyst of a catalytic converter, in situ, in a vehicle, the method comprising:

- (1) bringing a vehicle engine to working temperature;
- (ii) disconnecting the vehicle's fuel line from the engine;
- (iii) connecting the engine to a means for feeding a rejuvenating and/or cleaning composition thereto; and
- (iv). feeding the cleaning composition into the engine whilst the engine is running at a temperature high enough to effect cleaning of the catalyst.

The rejuvenating and/or cleaning is thus carried out, in situ, but whilst the engine fuel supply is disconnected from the engine, the engine being independently run on the composition.

Preferably the cleaning composition is fed into the injection system, through the combustion engine, through the catalytic converter and out through the exhaust system into the atmosphere.

Preferably the cleaning composition is combustible. Preferably the engine is run at a temperature of from 60 to 90°C, more preferably at or about the vehicle manufacturers recommended operating temperature

According to a further aspect of the present invention there is provided a rejuvenating and/or cleaning composition for a catalyst of a vehicle catalytic converter, comprising:

- i. at least one hydrocarbon source; and
- ii. at least one oxygen donor.

In some cases the oxygen donor and the hydrocarbon source can be one and the same compound.

Preferred compositions include one or more organic solvents as hydrocarbon source and/or oxygen donor. Examples include aliphatic alcohols e.g. iso propyl alcohol, ketones, e.g. acetone, aromatic hydrocarbons, e.g. xylene, aliphatic hydrocarbons, e.g. alkanes, paraffin (kerosene) and lamp oil. Clearly not all of the compounds are oxygen donors and the composition should include at least one oxygen donor.

A preferred composition comprises one or more organic solvents selected from isopropyl alcohol,

acetone, xylene and paraffin. The first two of these components are both oxygen donors and hydrocarbons.

Preferably the composition comprises all four of these ingredients.

Preferably the components of this mixture are present in the following amounts (by weight %)

	Preferred	More Preferred	Most Preferred
isopropyl alcohol	10-40%	15-25%	20%
acetone	10-40%	15-25%	20%
xylene	35-65%	45-55%	50%
paraffin	5-15%	7-12%	10%

The composition also preferably comprises one or more, and more preferably all of, the following trace elements:

Element	Symbol
Stronctium	Sr
Bismuth	Bi
Cadmium	Cd
Barium	Ba
Nickel	Ni
Manganese	Mn
Iron	Fe
Sodium	Na
Zinc	Zn
Aluminium	Al
Calcium	Ca
Copper	Cu
Lead	Pb
Colbalt	Co
Potassium	K
Chromium	Cr
Magnesium	Mo
Arsenic	As
Tin	Sn
Antimony	Sb
Vanadium	V
Titanium	Ti
Berillium	Be
Silicon	Si
Phosphorus	P
Tungsten	W
Molybdenum	Mo

These trace elements may each be present in an amount of \pm 30% of the figure shown for each trace element in the following table. A particularly preferred rejuvenating and/or cleaning composition includes one or more of the following trace elements in the amounts stated in the table:

Preferred % of trace elements

<u>Elements</u>	<u>%</u>
Selenium	0.01
Bismuth	0.01
Cadmium	0.01
Boron	0.01
Nickel	0.07
Manganese	0.05
Iron	0.16
Sodium	4.03
Zinc	0.05
Aluminum	0.19
Calcium	0.14
Copper	0.07
Lead	0.06
Colbalt	0.01
Potassium	15.59
Chromium	0.01
Manganese	0.05
Arsenic	0.05
Tin	0.14
Antimony	0.19
Vanadium	0.07
Titanium	0.01
Boronium	0.01
Silicon	0.19
Phosphorus	0.17
Tungsten	0.14
Molybdenum	0.01

Without wishing to be bound by theory it is believed that the composition functions because on

combustion it produces

- (i) oxygen which helps oxidise any carbonaceous layer present on the catalyst surface and which inhibits the function of the catalyst, and/or
- (ii) an organic acid (e.g. carboxylic acid) vapour which aids in cleaning the surface of the catalyst.

According to a further aspect of the present invention there is provided a rejuvenating and/or cleaning composition comprising a hydrocarbon source and an oxygen donor wherein said composition generates an organic acid, e.g. a carboxylic acid, vapour on combustion.

Although the invention is mainly for use with vehicles which run on unleaded fuel at least some of the compositions work with contamination caused by leaded fuels. For example lead contaminant has been removed from a catalyst in a catalytic converter using a composition of the invention.

The invention will be further described by way of example only with reference to the following example and test data.

Example 1.

An engine of a 1991 Nissan 300 ZX with 72,000 miles on the clock, and having a catalytic converter which had become poisoned, was run until the engine, and more importantly the exhaust system, reached normal operating temperature (approximately 80°C). The fuel

lines feeding the engine were then disconnected and in place of the fuel lines the engine was connected to an injection system purge machine and 1 litre of a rejuvenating and/or cleaning composition containing the following:

isopropyl alcohol	20%
acetone	20%
xylene	50%
paraffin	10%

and the trace elements listed in the Table above headed "preferred % of trace elements approximately in the amounts shown in the Table, was introduced under pressure into the engine. The machine circulated the composition (which is a liquid at room temperature) under pressure via the fuel injection system. The rejuvenating and/or cleaning composition burned in the engine and the combustion gases and any unburned fluid travelled over the catalyst of the catalytic converter.

In tests (analysis was by a calibrated four gas analyzer) the composition of example 1 was found to have a significant effect on tail pipe emissions as illustrated in Table 1.

Example 1

Table 1

	<u>Before *</u>	<u>After</u>
CO%	2.71	0.02
HC ppm	263	30

Example 2

Example 1 was repeated with a 1992 Vauxhall Astra with 80,000 miles on the clock. The results are set out in Table 2 below which indicates significant effect, on tail pipe emissions, of the rejuvenation and/or cleaning.

Table 2

	<u>Before *</u>	<u>After</u>
CO%	1.45	0.02
HC ppm	110	8

Example 3

Example 1 was repeated with a 1996 Renault Megane with 12,000 miles on the clock. The results are set out in Table 3 below which indicates significant effect, on tail pipe emissions, of the rejuvenation and/or cleaning.

Table 3

	<u>Before *</u>	<u>After</u>
CO%	0.00	0.01
HC ppm	72	27

* "Before" means - Before rejuvenating and/or cleaning with the composition of the invention.

Example 4

Example 1 was repeated with a Peugeot 605.

The results are set out in Table 4 below which indicates significant effect, on tail pipe emissions, of the rejuvenation and/or cleaning.

Example 5

Example 1 was repeated with a Ford Fiesta.

The results are set out in Table 5 below which indicates significant effect, on tail pipe emissions, of the rejuvenation and/or cleaning.

TABLE 4

	C0	CO ₂	HC	O ₂
Starting value	0.0072%	7.1%	36ppm	10.0%
after treatment	0.002%	13.6%	2ppm	7.6%

TABLE 5

	C0	CO ₂	HC	O ₂
Starting value	0.367%	15.3%	116ppm	2.5%
after treatment	0.023%	15.6%	49ppm	2.2%
follow up	0.030%	15.9%	63ppm	2.0%
follow up	0.008%	15.3%	23ppm	5.2%
follow up	0.081%		47ppm	

The "follow up" measurements were carried out approximately 1000 mile intervals.

These examples indicate that the catalyst is operating more effectively after treatment, indicating the catalyst has been rejuvenated and/or cleaned.

CLAIMS

1. A rejuvenating and/or cleaning composition for a catalyst of a vehicle catalytic converter, comprising:

- i. at least one hydrocarbon source; and
- ii. at least one oxygen donor.

2. A rejuvenating and/or cleaning composition comprising a hydrocarbon source and an oxygen donor wherein said composition generates an organic acid vapour on combustion.

3. A rejuvenating and/or cleaning composition as claimed in claim 2, wherein the organic acid vapour includes a carboxylic acid vapour.

4. A rejuvenating and/or cleaning composition as claimed in claim 1, 2 or 3, wherein the oxygen donor or one of the oxygen donors and the hydrocarbon source or one of the hydrocarbon sources are one and the same compound.

5. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims, including one or more organic solvents as hydrocarbon source and/or oxygen donor.

6. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents include aliphatic alcohols, ketones, aromatic hydrocarbons and/or aliphatic hydrocarbons.

7. A rejuvenating and/or cleaning composition as claimed in claim 5 or 6, wherein the one or more organic solvents include isopropyl alcohol.

8. A rejuvenating and/or cleaning composition as claimed in claim 5, 6 or 7, wherein the one or more organic solvents include acetone.

9. A rejuvenating and/or cleaning composition as claimed in any one of claims 5 to 8, wherein the one or more organic solvents include xylene.

10. A rejuvenating and/or cleaning composition as claimed in claim 5 or 6, wherein the one or more organic solvents include isopropyl alcohol, acetone and xylene.

11. A rejuvenating and/or cleaning composition as claimed in any one of claims 5 to 10, wherein the one or more organic solvents include alkanes, paraffin (kerosene) and/or lamp oil.

12. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents are selected from isopropyl alcohol, acetone, xylene and paraffin.

13. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims comprising isopropyl alcohol, acetone, xylene and paraffin.

14. A rejuvenating and/or cleaning

composition as claimed in claim 13, comprising 10-40 wt% isopropyl alcohol, 10-40 wt% acetone, 35-65 wt% xylene and 5-15 wt% paraffin.

15. A rejuvenating and/or cleaning composition as claimed in claim 13, comprising 15-25 wt% isopropyl alcohol, 15-25 wt% acetone, 45-55 wt% xylene and 7-12 wt% paraffin.

16. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims, comprising one or more trace elements selected from Sr, Bi, Cd, Ba, Ni, Mn, Fe, Na, Zn, Al, Ca, Cu, Pb, Co, K, Cr, Mg, As, Sn, Sb, V, Ti, Be, Si, P, W, and Mo.

17. A rejuvenating and/or cleaning composition as claimed in claim 16, wherein those trace elements which are present are each present in an amount of \pm 30% of the figure shown for the respective amount in the following table: Sr (0.01ppm), Bi (0.05ppm), Cd (0.01ppm), Ba (0.01ppm), Ni (0.07ppm), Mn (0.05ppm), Fe (0.16ppm), Na (4.03ppm), Zn (0.05ppm), Al (0.19ppm), Ca (0.14ppm), Cu (0.02ppm), Pb (0.06ppm), Co (0.01ppm), K (15.59ppm), Cr (0.01ppm), Mg (0.05ppm), As (0.05ppm), Sn (0.34ppm), Sb (0.10ppm), V (0.07ppm), Ti (0.01ppm), Be (0.01ppm), Si (0.39ppm), P (0.17ppm), W (0.14ppm), and Mo (0.01ppm).

18. The use of a rejuvenating and/or cleaning composition as defined in any one of claims 1

to 17 to rejuvenate and/or clean a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle.

19. A method of rejuvenating and/or cleaning a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle, said method comprising:

(i) bringing the catalytic converter up to working temperature; and then

(ii) passing a rejuvenating and/or cleaning composition as defined in any one of claims 1 to 17 into an engine of the vehicle whilst running the engine at idle.

20. A method as claimed in claim 19, wherein the rejuvenating and/or cleaning composition is passed into the vehicle engine under pressure.

21. A method of rejuvenating and/or cleaning a catalyst of a catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle, the method comprising:

(i) bringing an engine of the vehicle to working temperature;

(ii) disconnecting the vehicle's fuel line from the engine;

(iii) connecting the engine to a means for feeding a rejuvenating and/or cleaning composition thereto; and

(iv) feeding the cleaning composition into the engine whilst the engine is running at a temperature high enough to effect cleaning of the catalyst.

22. A method as claimed in claim 21, wherein the rejuvenating and/or cleaning composition is combustible.

23. A method as claimed in claim 21 or 22, wherein the rejuvenating and/or cleaning composition is as defined in any one of claims 1 to 17.

24. A method as claimed in any one of claims 19 to 23, wherein the rejuvenating and/or cleaning composition is fed into the injection system, through the engine, through the catalytic converter and out through the exhaust system into the atmosphere.

25. A method as claimed in any one of claims 19 to 24, comprising running the engine at a temperature of from 60 to 90°C.

26. A method as claimed in claim 25, comprising running the engine at or about the vehicle manufacturer's recommended operating temperature.

27. A rejuvenating and/or cleaning composition and/or a method substantially as hereinbefore described in any one of Examples 1 to 5.

Amendments to the claims have been filed as follows

1. A rejuvenating and/or cleaning composition for a catalyst of a vehicle catalytic converter, comprising:
 - i. at least one hydrocarbon source; and
 - ii. at least one oxygen donor.
2. A rejuvenating and/or cleaning composition comprising a hydrocarbon source and an oxygen donor wherein said composition generates an organic acid vapour on combustion.
3. A rejuvenating and/or cleaning composition as claimed in claim 2, wherein the organic acid vapour includes a carboxylic acid vapour.
4. A rejuvenating and/or cleaning composition as claimed in claim 1, 2 or 3, wherein the oxygen donor or one of the oxygen donors and the hydrocarbon source or one of the hydrocarbon sources are one and the same compound.
5. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims, including one or more organic solvents as hydrocarbon source and/or oxygen donor.
6. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents include aliphatic alcohols, ketones, aromatic hydrocarbons and/or aliphatic hydrocarbons.

7. A rejuvenating and/or cleaning composition as claimed in claim 5 or 6, wherein the one or more organic solvents include isopropyl alcohol.

8. A rejuvenating and/or cleaning composition as claimed in claim 5, 6 or 7, wherein the one or more organic solvents include acetone.

9. A rejuvenating and/or cleaning composition as claimed in any one of claims 5 to 8, wherein the one or more organic solvents include xylene.

10. A rejuvenating and/or cleaning composition as claimed in claim 5 or 6, wherein the one or more organic solvents include isopropyl alcohol, acetone and xylene.

11. A rejuvenating and/or cleaning composition as claimed in any one of claims 5 to 10, wherein the one or more organic solvents include alkanes, paraffin (kerosene) and/or lamp oil.

12. A rejuvenating and/or cleaning composition as claimed in claim 5, wherein the one or more organic solvents are selected from isopropyl alcohol, acetone, xylene and paraffin.

13. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims comprising isopropyl alcohol, acetone, xylene and paraffin.

14. A rejuvenating and/or cleaning

composition as claimed in claim 13, comprising 10-40 wt% isopropyl alcohol, 10-40 wt% acetone, 35-65 wt% xylene and 5-15 wt% paraffin.

15. A rejuvenating and/or cleaning composition as claimed in claim 13, comprising 15-25 wt% isopropyl alcohol, 15-25 wt% acetone, 45-55 wt% xylene and 7-12 wt% paraffin.

16. A rejuvenating and/or cleaning composition as claimed in any one of the preceding claims, comprising one or more trace elements selected from Sr, Bi, Cd, Ba, Ni, Mn, Fe, Na, Zn, Al, Ca, Cu, Pb, Co, K, Cr, Mg, As, Sn, Sb, V, Ti, Be, Si, P, W, and Mo.

17. A rejuvenating and/or cleaning composition as claimed in claim 16, wherein those trace elements which are present are each present in an amount of \pm 30% of the figure shown for the respective element in the following table: Sr (0.01ppm), Bi (0.05ppm), Cd (0.01ppm), Ba (0.01ppm), Ni (0.07ppm), Mn (0.05ppm), Fe (0.16ppm), Na (4.03ppm), Zn (0.05ppm), Al (0.19ppm), Ca (0.14ppm), Cu (0.02ppm), Pb (0.06ppm), Co (0.01ppm), K (15.59ppm) Cr (0.01ppm), Mg (0.05ppm), As (0.05ppm), Sn (0.34ppm), Sb (0.10ppm), V (0.07ppm), Ti (0.01ppm), Be (0.01ppm), Si (0.39ppm), P (0.17ppm), W (0.14ppm), and Mo (0.01ppm).

18. The use of a rejuvenating and/or cleaning composition as defined in any one of claims 1

to 17 to rejuvenate and/or clean a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle.

19. A method of rejuvenating and/or cleaning a catalyst in a vehicle catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle, said method comprising:

(i) bringing the catalytic converter up to working temperature; and then

(ii) passing a rejuvenating and/or cleaning composition as defined in any one of claims 1 to 17 into an engine of the vehicle whilst running the engine at idle.

20. A method as claimed in claim 19, wherein the rejuvenating and/or cleaning composition is passed into the vehicle engine under pressure.

21. A method of rejuvenating and/or cleaning a catalyst of a catalytic converter, in situ, in a vehicle i.e. without removal of the catalyst from the vehicle, the method comprising:

(i) bringing an engine of the vehicle to working temperature;

(ii) disconnecting the vehicle's fuel line from the engine;

(iii) connecting the engine to a means for feeding a rejuvenating and/or cleaning composition thereto; and

(iv) feeding the cleaning composition into the engine whilst the engine is running at a temperature high enough to effect cleaning of the catalyst.

22. A method as claimed in claim 21, wherein the rejuvenating and/or cleaning composition is combustible.

23. A method as claimed in claim 21 or 22, wherein the rejuvenating and/or cleaning composition is as defined in any one of claims 1 to 17.

24. A method as claimed in any one of claims 19 to 23, wherein the rejuvenating and/or cleaning composition is fed into the injection system, through the engine, through the catalytic converter and out through the exhaust system into the atmosphere.

25. A method as claimed in any one of claims 19 to 24, comprising running the engine at a temperature of from 60 to 90°C.

26. A method as claimed in claim 25, comprising running the engine at or about the vehicle manufacturer's recommended operating temperature.

27. A rejuvenating and/or cleaning composition and/or a method substantially as hereinbefore described in any one of Examples 1 to 5.



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Application No: GB 9800529.1
Claims searched: 1-27

Examiner: J.H. Warren
Date of search: 9 April 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.Q): B1E (EG); C5G (GAC)
Int CI (Ed.6): B01D 53/96; B01J 38/00; C10L 1/02; F01N 3/20
Other: ONLINE Databases: EPODOC, JAPIO and WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	EP 0 178 792 A2	GENERAL MOTORS - note use of a carboxylic acid	2,3
X	EP 0 166 006 A1	UNION RHEINISCHE BRAUNKOHLEN KRAFTSTOFF A.G.- the whole document is highly relevant, especially the examples	1-6,8,11
X	EP 0 070 619 A2	JOHNSON MATTHEY - see page 8 line 19 to page 9 line 3; note the use of hydrocarbons together with oxygen in the exhaust gas to regenerate the catalyst	1,18,19
X	WO 97/41336 A1 & GB 2 328 626 A	KOMATSU - see page 1 lines 17 - 24	1, 18, 19
X	US 5 316 558	GONZALEZ - see the compositions disclosed	1-6
X	US 4 265 638	BURKE - see composition exemplified	1,6-10
X	US 4 147 136	NIPPON SOKEN - see Column 6 line 59 to Column 7 line 37	1,18

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.

Hydrocarbon fuels contg. aq. ethanol - with sepn. prevented by addn. of ketone(s) and higher alcohol(s) obtd. by fermentation

Patent Assignee: INST FRANCAIS DU PETROLE

Inventors: BRIANT J; GUIBET J C; VANDECASTE J P

Patent Family

Patent Number	Kind	Date	Application Number	Kind	Date	Week	Type
FR 2493863	A	19820514				198226	B
SE 8106563	A	19820614				198226	
DE 3143654	A	19820708				198228	

Priority Applications (Number Kind Date): FR 8023919 A (19801107)

Patent Details

Patent	Kind	Language	Page	Main IPC	Filing Notes
FR 2493863	A		8		

Abstract:

FR 2493863 A

A fuel mixt. contains (wt.%): (a) 45-98.5 of an automobile gasoline, domestic fuel oil or gas oil: (b) 1-40 aq. ethanol, with a water content of 1-20, pref. 1-10, esp. 2-7; (c) 0.5-15 (pref. 1-7) of at least one additive from the group 4-10C alcohols and ketones. (c) is pref. a mixt. of 85-40 butanol and 15-60 acetone, or one of 50-85 butanol, 15-25 acetone and 5-35 isopropanol. Both these mixts. for (c) are obtainable by fermentation.

Used for replacement of automobile gasoline. Domestic fuel oil or gas oil. The octane number of gasoline is increased by adding (b). (c) permits aq. ethanol to be used without demixing caused by the water. Aq. ethanol is cheaper than ethanol.

Derwent World Patents Index

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**DEMANDE
DE BREVET D'INVENTION**

(21)

N° 80 23919

(54) Nouveaux carburants à base d'essence renfermant de l'éthanol hydraté et un additif.

(51) Classification internationale (Int. Cl. 3). C 10 L 1/18; C 12 N 1/22; C 12 P 7/16, 7/28.

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public de la demande B.O.P.I. — « Listes » n° 19 du 14-5-1982.

(71) Déposant : INSTITUT FRANÇAIS DU PETROLE, résidant en France.

(72) Invention de : Jean-Claude Guibet, Jean-Paul Vandecasteele et Jean Briant.

(73) Titulaire : *Idem* (71)

(74) Mandataire :

Les mélanges essence-alcools, gazole-alcools ou fuel-alcools ont déjà fait dans le passé et même récemment l'objet d'essais à titre de combustibles ou de carburants ; on sait, par exemple, que si l'on ajoute de l'éthanol à une essence, cela se traduit par l'obtention d'un carburant dont 5 l'indice d'octane est accru par rapport à l'indice d'octane de l'essence utilisée sans ajout de l'éthanol. Il en résulte qu'on peut utiliser, pour le mélange essence-alcool, un taux de compression plus élevé, conduisant à un meilleur rendement thermique du moteur. Toutefois des difficultés majeures apparaissent très rapidement en raison de la sensibilité à l'eau 10 des mélanges essence-alcool, fuel domestique-alcool ou gazole-alcool, la présence d'eau se traduisant par des phénomènes de démixtion. Il en résulte que, jusqu'à présent, il était absolument impératif d'utiliser de l'éthanol anhydre.

Or l'utilisation d'éthanol anhydre entraîne des dépenses d'investissement et d'énergie, notamment pour réaliser la distillation de l'éthanol, qui fait que pratiquement les mélanges essence -éthanol ou des mélanges similaires n'ont pas été utilisés sur une large échelle.

La présente demande de brevet rend possible l'utilisation d'éthanol non nécessairement anhydre, c'est-à-dire d'éthanol humide, pouvant renfermer jusqu'à 20% en poids d'eau. On conçoit alors l'intérêt de la présente invention qui va permettre d'utiliser, en mélange avec de l'essence automobile ou avec un fuel domestique ou un gazole, de l'éthanol à bon marché, utilisable sans fractionnement ou distillation poussée et coûteuse, par exemple de l'éthanol à 95%, ou plus dilué (par exemple, éthanol des betteraves 25 ravières ou d'autres types de cultures).

L'invention concerne ainsi un nouveau carburant qui comprend :

- a) de l'éthanol hydraté,
- b) une fraction d'hydrocarbures, telle que essence, gazole ou fuel domestique,

30 et c) un additif qui a pour rôle d'assurer la miscibilité de l'alcool hydraté et de la fraction d'hydrocarbures, sans modifier sensiblement des autres propriétés du carburant. En particulier l'indice d'octane, en cas d'emploi d'essence, se trouve généralement accru.

Cet additif est généralement un alcool ayant au moins 4 atomes de carbone ou une cétone, ou un mélange des deux. On préfère un mélange d'alcool butylique et d'acétone. Ce mélange renferme en poids, de préférence, 85 à 40% d'alcool butylique et 15 à 60% d'acétone. De préférence, l'additif est un mélange d'alcool butylique, d'acétone et d'isopropanol. Plus particulièrement, on peut utiliser un mélange renfermant, en poids, 50 à 85% d'alcool butylique, 15 à 25% d'acétone et 5 à 35% d'isopropanol.

Selon l'invention l'additif peut être encore, par exemple, un alcool ou un mélange d'alcools renfermant 4 à 10 atomes de carbone par molécule.

Conformément à l'invention, les nouveaux carburants peuvent renfermer en poids :

(a) 45 à 98,5% d'essence automobile ou d'un gazole ou d'un fuel oil domestique,

(b) 1 à 40% d'éthanol hydraté (et de préférence 5 à 20%, notamment quand cet alcool hydraté est destiné à être mélangé à une essence "ordinaire" ou "super" pour automobile) dans lequel la teneur en eau, en poids, est comprise entre 1 et 20%, de préférence entre 1 et 10% et plus particulièrement entre 2 et 7%.

(c) 0,5 à 15% de l'additif défini ci-dessus et de préférence 1 à 20 7% de cet additif.

Pour une concentration donnée de l'essence, du fuel oil ou du gazole et pour une concentration donnée de l'éthanol hydraté, la proportion optimale de l'additif dépend essentiellement des minima de la température ambiante dans le pays d'utilisation du carburant. Par exemple, pour des minima de l'ordre de -30°C, la concentration suffisante en un mélange alcool butylique-acétone (75% en poids de butanol technique contenant moins de 1% d'impuretés et 25% en poids d'acétone technique contenant moins de 0,5% d'impuretés) est de l'ordre de 6 à 7% en poids pour obtenir un carburant à partir d'un mélange : essence : 90% en poids éthanol à 95% : 10% en poids.

Cette teneur de 6 à 7% en mélange alcool butylique-acétone, reste valable si le véhicule, utilisant un tel carburant, se déplace ensuite dans des régions moins froides, ou si la température se réchauffe. Vers + 10°C. en fait, une concentration de l'ordre de 3% en additif, suffirait.

L'essence utilisée, dans l'exemple ci-dessus, ainsi que dans les exemples présentés ci-après, avait la composition suivante :

5	Densité à 15°C : 0,742
	Teneur en oléfines : 16,5 % en poids
	Teneur en aromatiques : 29,0 % en poids
	Teneur en hydrocarbures saturés : 54,5 % en poids
	Intervalle de distillation : 35°C - 185°C

Inversement, si l'on se fixe une teneur déterminée en additif dans 10 le carburant, il est alors possible de faire varier le pourcentage d'éthanol et/ou la teneur en eau de l'éthanol utilisé.

Les proportions d'additifs données ci-dessus constituent de simples exemples de mise en œuvre de l'invention, et il est clair qu'il est aisé de déterminer, dans chaque cas particulier, par un essai préalable simple, 15 la proportion minimale d'additif qui permet d'obtenir un mélange satisfaisant. En règle générale, plus la teneur en eau de l'éthanol sera grande, ou plus la proportion de cet éthanol sera élevée, et plus on devra utiliser d'additif.

Les mélanges alcool butylique-acétone ou alcool butylique-acétone-isopropanol peuvent être préparés par tout moyen adéquat. Ils peuvent notamment être obtenus par fermentation productrice du mélange alcool butylique-acétone ou alcool butylique-acétone-isopropanol, ladite fermentation étant effectuée sur un hydrolysat d'un substrat cellulosique.

Ainsi on peut obtenir plus précisément ces mélanges par un procédé consistant à hydrolyser au moins un substrat cellulosique au moyen d'un enzyme cellulolytique, de façon à obtenir un hydrolysat et à effectuer ensuite une fermentation dudit hydrolysat.

La production d'enzymes cellulolytiques peut être réalisée par culture 30 d'un champignon appartenant de préférence aux genres Sporotrichum, Polyporus, Fusarium, Penicillium, Myrothecium et Trichoderma ou d'une bactérie appartenant de préférence au genre Clostridium.

Les substrats cellulaires sont, par exemple, ceux obtenus après prétraitement de vieux papiers, de paille de céréales, de bagasse, de rafles et tiges de maïs ou de déchets de scierie ou forestiers de bois feuillus et de résineux. Ces prétraitements peuvent être mécaniques (broyage 5 par exemple) et/ou chimiques (par exemple par traitement à la soude, de préférence avec environ 6% en poids de soude/poids de substrats). L'hydrolyse du substratcellulosique en sucres (réaction enzymatique) est réalisée selon les moyens habituels, de préférence entre 30 et 60°C à un pH compris généralement entre 3,5 et 6,5, ces conditions opératoires dépendant essentiellement de la nature du système enzymatique. 10

Sur les hydrolysats ainsi obtenus, supplémentés en éléments nutritifs, on effectue la fermentation désirée. Les organismes utilisés sont des bactéries, appartenant de préférence au genre Clostridium. La fermentation est effectuée de façon anaérobie à une température comprise généralement entre 25 et 40°C et à un pH généralement compris entre 4 et 7,5. 15

Les facteurs qui influent sur la composition des mélanges obtenus sont la souche utilisée, le substrat et les conditions de fermentation, c'est-à-dire le pH, la température, la composition du milieu, notamment la source d'azote ; plus précisément, les organismes utilisés pour la fermentation acétone/butanol, sont des bactéries qui appartiennent généralement au genre Clostridium. Les espèces utilisées ont été décrites sous les noms de Clostridium saccharoacetobutylicum, Clostridium acetobutylicum, Clostridium saccharobutyl aceticum, Clostridium saccharoperbutylicum. L'espèce type est Clostridium acetobutylicum. 20

Les organismes utilisés pour la fermentation butanol/isopropanol, qui sont proches des précédents, appartiennent aussi au genre Clostridium. Les espèces utilisées ont été décrites sous les noms de Clostridium propylbutylicum, Clostridium visci fasciens mais les espèces types préférées dans la présente invention sont Clostridium butylicum, ainsi que Clostridium beijerinckii et Clostridium toanum. 30

EXEMPLES

A titre d'exemples, on a préparé plusieurs carburants, qui, tous, sauf celui de l'exemple comparatif n° 1 ont donné satisfaction aux températures auxquelles ils ont été utilisés.

EXEMPLE 1 (comparatif)

Un mélange à 85% d'une essence de composition donnée ci-dessus et à 15% d'éthanol "95" ne donne pas un carburant homogène et est donc inutilisable.

5 EXEMPLES 2 à 5

On a utilisé l'essence de composition donnée ci-dessus.

Le premier mélange utilisé renfermait, en poids :

83% d'essence,

15% d'éthanol "95",

10 et 2% d'un mélange (en poids) à 75% d'alcool butylique industriel et 25% d'acétone industrielle.

Le deuxième mélange utilisé renfermait, en poids :

71,2% d'essence,

17,8% d'éthanol "90" c'est-à-dire renfermant 10% d'eau,

15 et 11% d'un mélange (en poids) à 75% d'alcool butylique et 25% d'acétone technique.

Le troisième mélange utilisé renfermait en poids :

90% d'essence,

5% d'éthanol "95",

20 et 5% du mélange (en poids) à 75% d'alcool butylique et 25% d'acétone technique.

Le quatrième mélange utilisé renfermait en poids :

90% d'essence,

5% d'éthanol "95"

25 et 5% du mélange (en poids) à 70% d'alcool butylique, 15% d'acétone et 15% d'isopropanol.

Les mélanges des exemples 2 à 5 ont été utilisés à des températures variées, dans des voitures automobiles de type classique, et ont donné des résultats entièrement satisfaisants. Les départs à froid ont toujours été faciles et aucun cliquetis n'a été observé.

REVENDEICATIONS

- 1.- Nouveau carburant renfermant en poids :
 - (a) 45 à 98,5% d'une essence automobile ou d'un fuel oil domestique ou d'un gazole,
 - (b) 1 à 40% en poids d'éthanol hydraté dans lequel la teneur en eau, en poids, est comprise entre 1 et 20%,
 - (c) 0,5 à 15% d'au moins un additif qui est choisi dans le groupe constitué par les alcools renfermant de 4 à 10 atomes de carbone par molécule et les cétones.
- 2.- Nouveau carburant selon la revendication 1 renfermant 5 à 20% d'éthanol hydraté dans lequel la teneur en eau, en poids, est comprise entre 1 et 10%.
- 3.- Nouveau carburant selon la revendication 1 dans lequel l'additif est un mélange d'alcool butylique et d'acétone, ledit mélange renfermant, en poids, 85 à 40% d'alcool butylique et 15 à 60% d'acétone.
- 4.- Nouveau carburant selon la revendication 1 dans lequel l'additif est un mélange alcool butylique-acétone-isopropanol, ledit mélange renfermant, en poids, 50 à 85% d'alcool butylique, 15 à 25% d'acétone et 5 à 35% d'isopropanol.
- 5.- Nouveau carburant selon l'une des revendications 1 à 4 dans lequel la teneur en additif est comprise entre 1 et 7% en poids.
- 6.- Procédé pour l'obtention d'un nouveau carburant selon l'une des revendications 3 et 4 dans lequel ledit mélange est obtenu par fermentation alcool butylique-acétone ou alcool butylique-acétone-isopropanol, ladite fermentation étant effectuée sur un hydrolysat d'un substrat cellulosique.
- 7.- Procédé selon la revendication 6 dans lequel ledit mélange est obtenu par un procédé consistant à hydrolyser au moins un substrat cellulosique au moyen d'enzymes cellulolytiques, de façon à obtenir un hydrolysat, et à effectuer ensuite une fermentation dudit hydrolysat.

8.- Procédé selon la revendication 7 dans lequel des enzymes cellulolytiques résultent de la culture préalable d'une bactérie appartenant au genre Clostridium, ou d'un champignon appartenant aux genres Sporotrichum, Polyporus, Penicillium, Fusarium, Myrothecium et Trichoderma.

5 9.- Procédé selon la revendication 7, appliqué à la fermentation acétono-butylique, caractérisé en ce qu'on effectue la fermentation de l'hydrolysat en présence d'au moins une bactérie du genre Clostridium choisie dans le groupe constitué par les espèces :

- 10 . Clostridium saccharoacetobutylicum,
- . Clostridium acétobutylicum,
- . Clostridium saccharobutyl acétonicum,
- et . Clostridium saccharoperbutylicum.